

A Study on Advanced Lithium-Based Battery Cell Chemistries to Enhance Lunar Exploration Missions

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NASA's Exploration Technology Development Program (ETDP) Energy Storage Project conducted an advanced lithium-based battery chemistry feasibility study to determine the best advanced chemistry to develop for the Altair Lunar Lander and the Extravehicular Activities (EVA) advanced Lunar surface spacesuit. These customers require safe, reliable energy storage systems with extremely high specific energy as compared to today's state-of-the-art batteries. Based on customer requirements, the specific energy goals for the development project are 220 watt-hours per kilogram (Wh/kg) delivered at the battery level at 0 degrees Celsius ($^{\circ}\text{C}$) at a C/10 discharge rate. Continuous discharge rates between C/5 and C/2, operation over 0 to 30 degrees $^{\circ}\text{C}$, and 200 cycles are targeted.

The team, consisting of members from NASA Glenn Research Center, Johnson Space Center, and Jet Propulsion Laboratory, surveyed the literature, compiled information on recent materials developments, and consulted with other battery experts in the community to identify advanced battery materials that might be capable of achieving the desired results with further development. A variety of electrode materials were considered, including layered metal oxides, spinel oxides, and olivine-type cathode materials, and lithium metal, lithium alloy, and silicon-based composite anode materials. Lithium-sulfur systems were also considered. Hypothetical cell constructs that combined compatible anode and cathode materials with suitable electrolytes, separators, current collectors, headers, and cell enclosures were modeled.

While some of these advanced materials are projected to obtain the desired electrical performance, there are risks that also factored into the decision making process. The risks include uncertainties due to issues such as safety of a system containing some of these materials, ease of scaling-up of large batches of raw materials, adaptability of the materials to processing using established or reasonable cost manufacturing techniques, manufacturability of the materials in dimensions required for integration into battery cells of practical capacities, low Technology Readiness Levels (TRL), and the ability to achieve the desired performance by the customer need dates. The advanced cell chemistry options were evaluated with respect to multiple quantitative and qualitative attributes while considering their projected performance at the end of the available development timeframe. Following a rigorous ranking process, a chemistry that combines a lithiated nickel manganese cobalt oxide (Lithium NMC) cathode with a silicon-based composite anode was selected as the technology that can offer the best combination of safety, specific energy, energy density, and likelihood of success.

Tasks over the next three years will focus on development of electrode materials, compatible electrolytes, and separator materials, and integration of promising components to assess their combined performance in working cells. Cells of the chosen chemistry will be developed to TRL 6 by 2014 and will then be transferred to the customers for infusion into their mission paths.



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11th Electrochemical R&D Symposium

Pier V Hotel

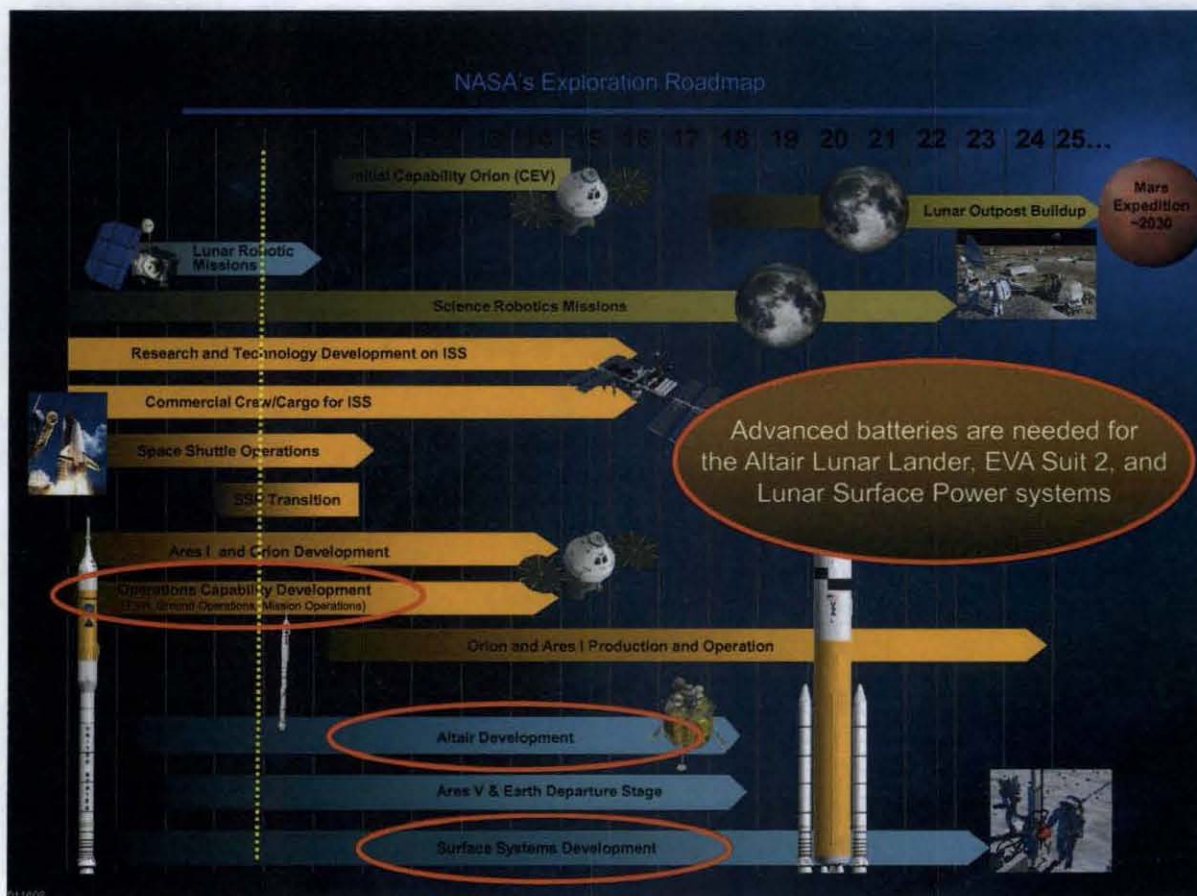
Baltimore, MD

July 13-16th, 2009

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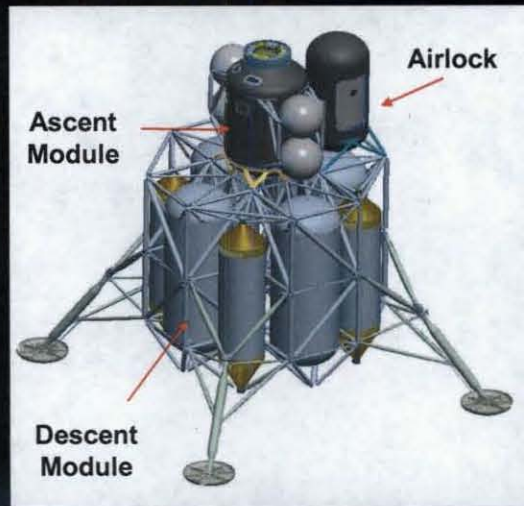


Altair Ascent Stage Power

Preliminary Nominal Power Requirements:*

Human safe, reliable operation

- 22.7 kWhr energy, delivered
- 1.67 kW average and 2 kW peak power
- Mass allocation: 121.6 kg
- Volume allocation: 85 liters
- 7 hours continuous operation
- 1 cycle (10 cycles desired)
- Operation over 0 – 30 degrees C
- Operation in 0 – 1 G



* LDAC - 3

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Lunar EVA Suit Power

Advanced Li-ion batteries will be used to provide power for the PLSS, Communications, Avionics, and Informatics system, helmet, heater, camera, and biomedical sensors.

Preliminary Power Requirements:

- Human safe, reliable operation
- 1155 Whr energy, delivered
- 145 W average and 233 W peak power
- Mass allocation: 5 kg
- Volume allocation: 3 liters
- 8 hour operation per sortie
- 100 cycles (operation every other day for 6 mos.)
- Operation over 0 – 30 degrees C

Compared to current PLSS:

- 134% increase in energy requirement
- 106% increase in average power requirement
- 33% increase in peak power requirement
- >7x increase in cycle life requirement
- 25% decrease in mass allocation



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Lunar Surface Systems Mobility Systems Rovers

Preliminary Power Requirements:

Human safe, reliable operation

- >150 Wh/kg delivered
- 100-1000 cycles
- Operation over 0 – 30 degrees C
- Maintenance-free operation



- Actual operating environment can range from -233 deg C in permanently dark craters to +120 deg C at the equator.
- Trade studies underway to assess merit of extending battery operating temperature range to -55 to 60 deg C versus designing the rover thermal system to keep battery within 0 – 30 degrees C.



Energy Storage Project Lithium-Ion Cell Development

Two parallel cell development approaches to meet Constellation customer requirements

- High Energy Cell Development
 - Safe, reliable Li-ion cell with improved specific energy and energy density over SOA and good cycle life
 - Combination of newly developed cathode, electrolyte, separator and safety components with a carbonaceous anode with known heritage and performance
- Ultra High Energy Cell Development
 - Safe, reliable Li-ion system with greatly improved specific energy and energy density over SOA and low cycle life
 - Very high energy system for applications where mass and volume reduction is enabling and cycle requirements are benign
 - Combination of newly developed anode, cathode, electrolyte, separator and safety components
 - Higher developmental risk than High Energy Cell
 - Much higher gains in component level specific capacity over conventional electrode materials required for success
 - Addition of a developmental anode increases risk in areas of electrochemical performance, sufficient maturity by need dates, and scalability and manufacturability.
 - Higher energy chemistry and Li metal and Li alloy anodes are inherently less safe – component-level inherent safety features more critical



Feasibility Study to Determine Ultra High Energy Chemistry

Customers' top priority is safety.

Based on customer requirements, team determined safety goals:

No fire or thermal runaway at the component level

No chemistry exists that can meet customers' aggressive specific energy goals. Desire for a safer chemistry presents a set of conflicting objectives – Safer chemistry combined with ultra high specific energy

Feasibility study was initiated to determine the best advanced chemistry to meet EVA and Altair's requirements on the established schedule (in time for customer System Design Reviews) and within available resources.

Goal of Feasibility Study:

Determine the best advanced chemistry to develop for EVA and Altair who require safe, reliable energy storage systems with extremely high specific energy as compared to today's state-of-the-art (SOA) batteries.

Advanced chemistries were researched and evaluated against attributes that characterized each of the chemistries

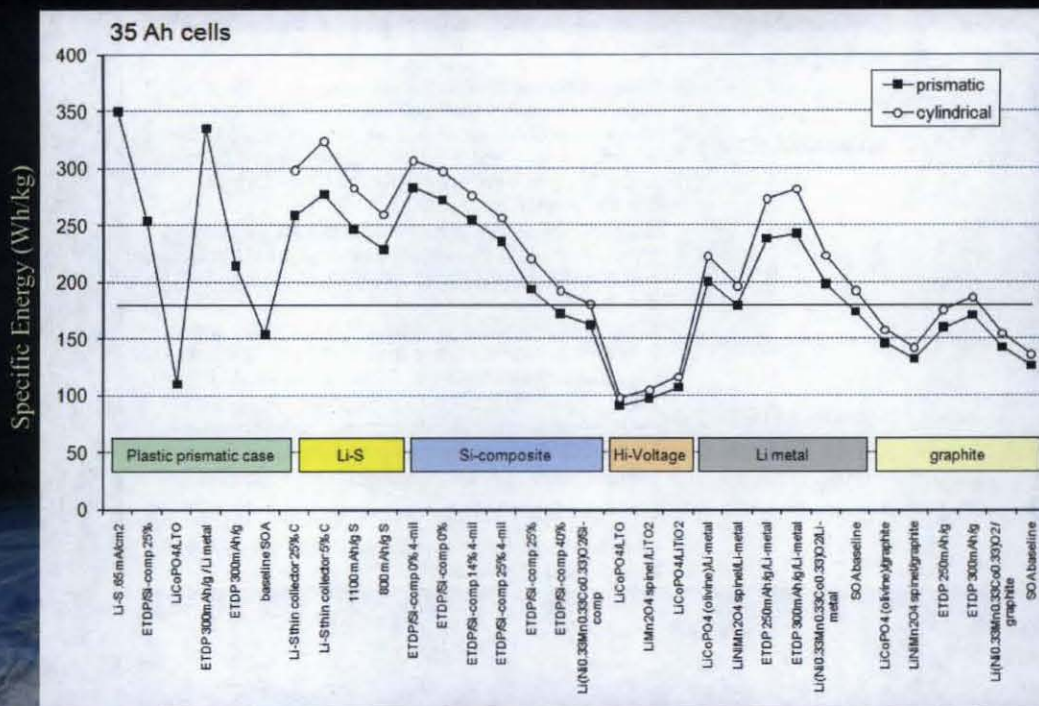


Attributes for Ranking Chemistries

Attribute	Definitions
Cost to TRL 6	The cost to develop the technology to TRL 6, including costs attributed to costly manufacturing processes or processes that cannot be automated
Cycle Life	Projected cycle life of the technology
Energy Density	Projected energy density of the technology (calculated under a standard set of conditions)
Manufacturability	The projected level of ease or difficulty associated with working with materials, scaling up batches of materials, and manufacturing cells of practical capacity made from these components, and the projected adaptability of materials to large scale processing
Rate Capability up to C/5	Likelihood that the technology can meet a C/5 continuous discharge rate
Rate Capability up to C/2	Likelihood that the technology can meet a C/2 continuous discharge rate
Safety	The likelihood that a cell made from these components can be made to be safe. Included safety under normal operation and abuse conditions
Schedule	Likelihood that TRL 6 cells can be delivered by March 2104
Specific Energy	Projected specific energy of the technology (calculated under a standard set of conditions)
Storage and Calendar Life	Projected storage + calendar life, where calendar life includes the operating time plus periods at open circuit between active charging and discharging



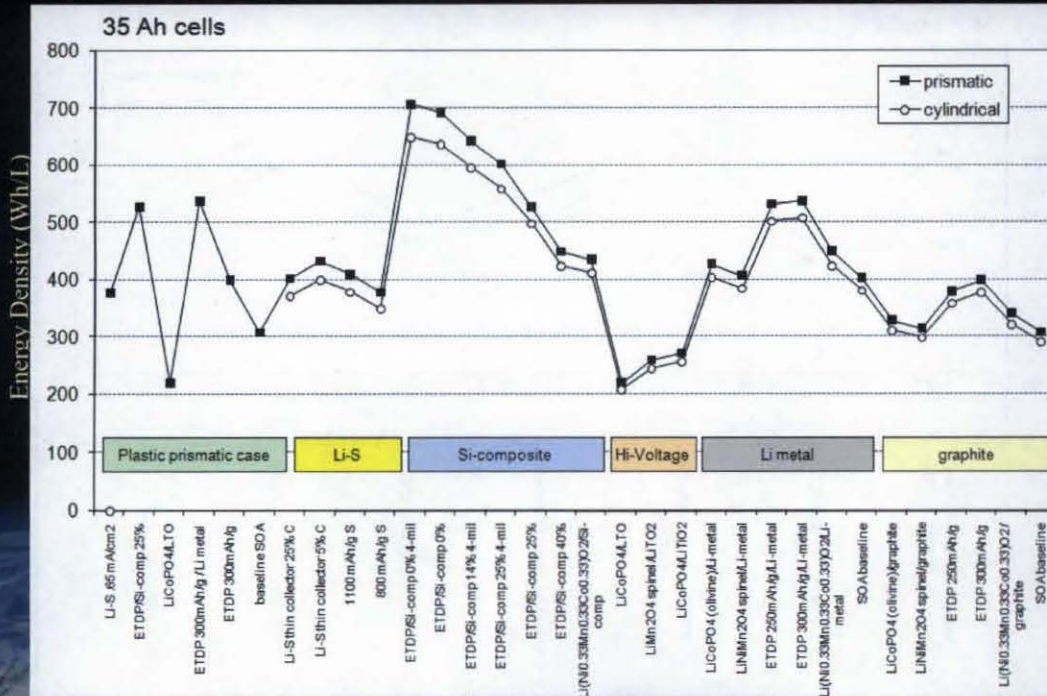
Project Specific Energy for Chemistry Options



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Projected Energy Density for Chemistry Options



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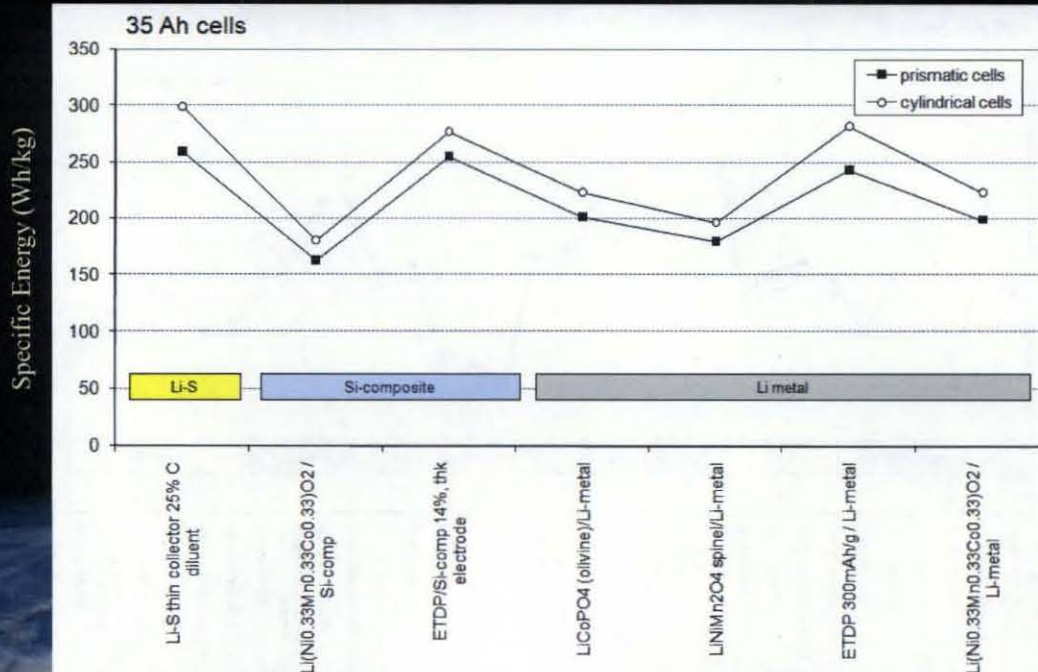


Final Chemistry Options

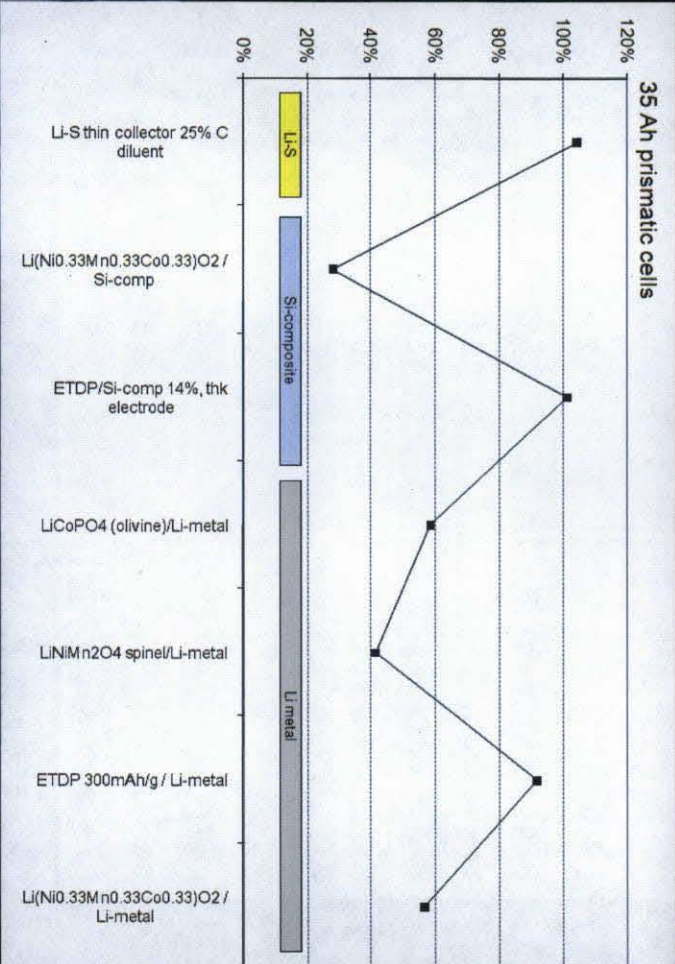
Anode	Cathode	Description
Si-Composite	$\text{Li}(\text{LiMnCo})\text{O}_2$ (ETDP)	Si-based composite anode with 1000 mAh/g specific capacity and 14% irreversible capacity. Lithiated nickel manganese cobalt oxide layered cathode with 300 mAh/g specific capacity and 4 mil electrode thickness. Cathode currently under development for the ETDP Energy Storage project.
Si-Composite	$\text{Li}(\text{Ni}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33})\text{O}_2$	Si-based composite anode with 1000 mAh/g specific capacity and 14% irreversible capacity. Nickel manganese cobalt oxide cathode (commercial "one third, one third, one third" formulation).
Li-metal	$\text{Li}(\text{Ni}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33})\text{O}_2$	Li-metal anode. Nickel manganese cobalt oxide cathode (commercial "one third, one third, one third" formulation).
Li-metal	$\text{Li}(\text{LiMnCo})\text{O}_2$ (ETDP)	Li-metal anode. Lithiated nickel manganese cobalt oxide layered cathode with 300 mAh/g specific capacity and 4 mil thick electrode. Cathode currently under development for the ETDP Energy Storage project.
Li-metal	$\text{LiNiMn}_2\text{O}_4$	Li-metal anode. $\text{LiNiMn}_2\text{O}_4$ cathode, spinel structure.
Li-metal	LiCoPO_4	Li-metal anode. LiCoPO_4 , olivine structure.
Li-metal	$(\text{Li}_2)\text{S}$	Li-metal anode. Sulfur cathode with 1100 mAh/g specific capacity and 25% diluent.



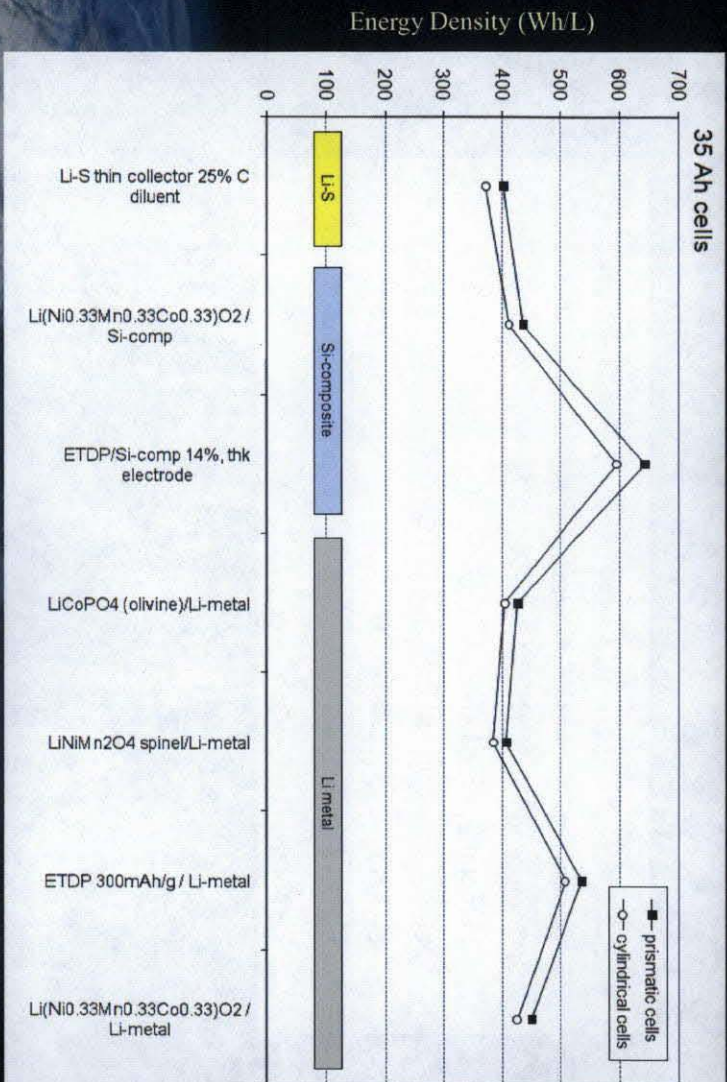
Projected Specific Energy for Final Options



Projected Percent Gain in Specific Energy of Final Chemistry Options over Li-ion State-of-the-Art Aerospace Cells (MER rover)



Projected Energy Density for Final Options





Attribute Weightings with respect to their Importance in an Advanced Chemistry

Attribute	Final Weight
Safety	17.9
Rate Capability up to C/5	15.6
Specific Energy	15.0
Storage and Calendar Life	12.2
Energy Density	10.2
Manufacturability	8.3
Schedule	8.0
Cost to TRL 6	6.5
Cycle Life	3.8
Rate Capability up to C/2	2.5

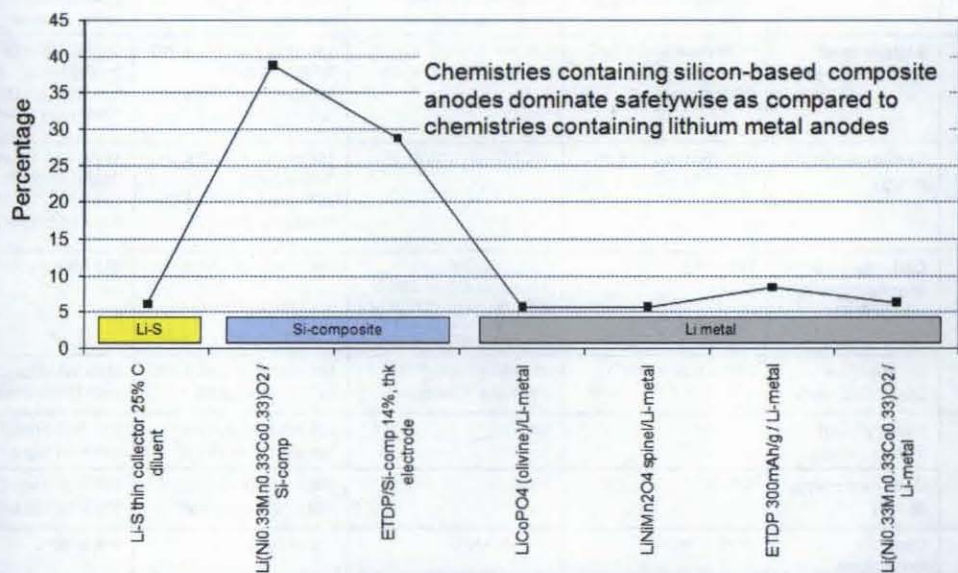


Safety Weightings

Anode	Cathode	Weight
Si-Composite	Li(LiNMC)O ₂ (ETDP)	28.8
Si-Composite	Li(Ni _{0.33} Mn _{0.33} Co _{0.33})O ₂	38.9
Li-metal	Li(Ni _{0.33} Mn _{0.33} Co _{0.33})O ₂	6.3
Li-metal	Li(LiNMC)O ₂ (ETDP)	8.4
Li-metal	LiNiMn ₂ O ₄	5.7
Li-metal	LiCoPO ₄	5.7
Li-metal	(Li ₂)S	6.1



Safety Weightings



Individual weights add up to 100 – graph shows percentage out of 100



Final Weights and Chemistry Selection

Anode	Cathode	Final Weight
Si-Composite	Li(Ni _{0.33} Mn _{0.33} Co _{0.33})O ₂	20.2
Si-Composite	Li(LiNMC)O ₂ (ETDP)	17.0
Li-metal	LiNiMn ₂ O ₄	15.3
Li-metal	Li(Ni _{0.33} Mn _{0.33} Co _{0.33})O ₂	13.9
Li-metal	Li(LiNMC)O ₂ (ETDP)	13.1
Li-metal	(Li ₂)S	11.5
Li-metal	LiCoPO ₄	9.1

- Li(NMC) cathode with Si-based composite anode offers:
 - Higher safety, manufacturability and rate capability
 - Lower specific energy
- ETDP cathode with Si-based composite anode offers:
 - Higher specific energy
 - Lower safety, manufacturability and demonstrated rate capability

ETDP cathode with Si-based composite anode chosen as Ultra High Energy chemistry due to its potential to achieve much higher specific energy.

Key Performance Parameters for Battery Technology Development



Customer Need	Performance Parameter	State-of-the-Art	Current Value	Threshold Value	Goal
Safe, reliable operation	No fire or flame	Instrumentation/control-ers used to prevent unsafe conditions. There is no non-flammable electrolyte in SOA	Preliminary results indicate a moderate reduction in the performance with flame retardants and non-flammable electrolytes	Benign cell venting without fire or flame and reduce the likelihood and severity of a fire in the event of a thermal runaway	Tolerant to electrical and thermal abuse such as over-temperature, over-charge, reversal, and external short circuit with no fire or flame
Specific energy Lander: 150 – 210 Wh/kg 10 cycles Rover: 160 – 200 Wh/kg EVA: 270Wh/kg 100 cycles	Battery-level specific energy*	90 Wh/kg at C/10 & 30°C 83 Wh/kg at C/10 & 0°C (MER rovers)	130 Wh/kg at C/10 & 30°C 120 Wh/kg at C/10 & 0°C	135 Wh/kg at C/10 & 0°C "High-Energy**" 150 Wh/kg at C/10 & 0°C "Ultra-High Energy***"	150 Wh/kg at C/10 & 0°C "High-Energy" 220 Wh/kg at C/10 & 0°C "Ultra-High Energy"
	Cell-level specific energy	130 Wh/kg at C/10 & 30°C 118 Wh/kg at C/10 & 0°C	150 Wh/kg at C/10 & 0°C	165 Wh/kg at C/10 & 0°C "High-Energy" 180 Wh/kg at C/10 & 0°C "Ultra-High Energy"	180 Wh/kg at C/10 & 0°C "High-Energy" 260 Wh/kg at C/10 & 0°C "Ultra-High Energy"
	Cathode-level specific capacity Li(Li,NiMn)O ₂	180 mAh/g	Li(Li _{0.17} Ni _{0.25} Mn _{0.58})O ₂ : 240 mAh/g at C/10 & 25°C Li(Li _{0.2} Ni _{0.13} Mn _{0.54} Co _{0.13})O ₂ : 250 mAh/g at C/10 & 25°C 200 mAh/g at C/10 & 0°C	260 mAh/g at C/10 & 0°C	280 mAh/g at C/10 & 0°C
	Anode-level specific capacity	280 mAh/g (MCMB)	350 mAh/g (MPG-111) 450 mAh/g Si composite	600 mAh/g at C/10 & 0°C (with Si composite)	1000 mAh/g at C/10 0°C (with Si composite)
Energy density Lander: 311 Wh/l Rover: TBD EVA: 400 Wh/l	Battery-level energy density	250 Wh/l	n/a	270 Wh/l "High-Energy" 360 Wh/l "Ultra-High"	320 Wh/l "High-Energy" 420 Wh/l "Ultra-High"
	Cell-level energy density	320 Wh/l	n/a	385 Wh/l "High-Energy" 460 Wh/l "Ultra-High"	390 Wh/l "High-Energy" 530 Wh/l "Ultra-High"
Operating environment 0°C to 30°C, Vacuum	Operating temperature	-20°C to +40°C	-50°C to +40°C	0°C to 30°C	0°C to 30°C

Assumes prismatic cell packaging for threshold values. Goal values include lightweight battery packaging.

* Battery values are assumed at 100% DOD, discharged at C/10 to 3,000 volts/cell, and at 0°C operating conditions

** "High-Energy" = Exploration Technology Development Program cathode with MCMB graphite anode

*** "Ultra-High Energy" = Exploration Technology Development Program cathode with Silicon composite anode

National Aeronautics and Space Administration



Energy Storage Project Li-ion Cell Development

Component-level goals will be addressed thorough a combination of NASA in-house materials development efforts and NASA Research Announcement contracts

- Materials developed will be delivered to NASA and screened for their electrochemical and thermal performance, and compatibility with other candidate cell components
- Other activities funded through NASA can be leveraged – NASA Small Business Innovative Research (SBIR) Program and Innovative Partnership Program (IPP)
- Leveraging of other government programs (DOD, DOE) for component-level technology



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NASA Research Announcement NNC08ZP022N

Research and Development of Battery Cell Components

• Contracts Awarded

- Georgia Tech Research Corp. & Clemson University, "Design of Resilient Silicon Anodes"
- Lockheed Martin Space Systems Company, "Advanced Nanostructured Silicon Composite Anode Program"
- University of Texas at Austin, "Development of High Capacity Layered Oxide Cathodes"
- NEI Corp., "Mixed Metal Composite Oxides for High Energy Li-ion Batteries"
- Yardney, "Flame-retardant, Electrochemically Stable Electrolyte for Lithium-ion Batteries"
- Giner, "Control of Internal and External Short Circuits in Lithium-Ion Batteries"
- Physical Sciences, "Metal Phosphate Coating for Improved Cathode Material Safety"



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SBIRs and STTRs

• Phase I SBIRS

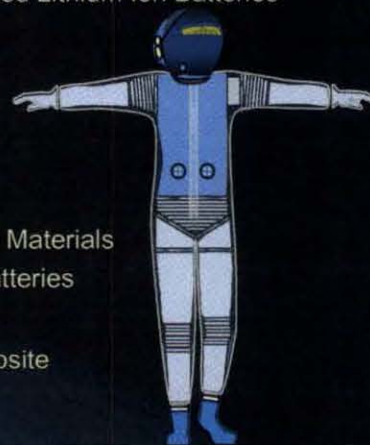
- Yardney Technical Products –Advanced Battery Materials for Rechargeable Advanced Space-Rated Li-Ion Batteries
- Superior Graphite Co. –SiLix-C Nanocompositesfor High Energy Density Li-ion Battery Anodes
- Physical Sciences, Inc. –Silicon Whisker and Carbon Nanofiber Composite Anode
- TH Chem, Inc. –New Li Battery Chemistry for Improved Performance
- TDA Research, Inc. --High Capacity Anodes for Advanced Lithium Ion Batteries
- EIC Laboratories, Inc. –Nanoshell Encapsulated Li-ion Battery Anodes for Long Cycle Life
- Giner, Inc. – Non-Flammable, High Voltage Electrolytes for Lithium Ion Batteries

• Phase II SBIR –

- Yardney Technical Products – Nano-Engineered Anode Materials for Rapid Recharge High Energy Density Lithium-ion Batteries

• STTR -

- NEI Corporation - High capacity and high voltage composite oxide cathode for Li-ion batteries



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